

CHROMIUM HEXAVALENT COMPOUNDS

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CARCINOGENICITY

Chromium hexavalent compounds are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans occupationally exposed in the chromate production, chromate pigment production, and chromium plating industries (IARC 1987, 1990). An increased incidence of lung cancer has been observed among workers in both the bichromate producing industry and chromate-pigment manufacturing. There is evidence of a similar risk among chromium platers and chromium-alloy workers. The incidences of cancers at other sites may also be increased in such populations; however, a clear distinction between the relative carcinogenicity of chromium compounds of different oxidation states or solubilities has been difficult to achieve. Recent studies of chromate-pigment makers and users, chrome platers, welders, and chrome-alloy foundry workers have shed some light on this problem. For chromate-pigment makers and users, respiratory cancer excesses have generally been found. Chromium pigments are typically hexavalent and commonly include zinc, lead, or strontium chromate. Chrome platers have also been found to have excess lung cancer. Stainless steel welding involves the greatest exposure to hexavalent chromium, as well as to nickel, and one study of chromium-nickel alloy foundry workers showed a statistically significant excess of lung cancers.

An IARC Working Group reported that there is sufficient evidence of carcinogenicity of calcium chromate (CAS No. 13765-19-0), lead chromate (CAS No. 7758-97-6), strontium chromate (CAS No. 7789-06-2), and zinc chromate (CAS No. 13530-65-9); and limited evidence for the carcinogenicity of chromium trioxide (CAS No. 1333-82-0) and sodium dichromate (CAS No. 10588-01-9) in experimental animals (IARC 1973, 1980, 1982, 1987, 1990). Calcium chromate produced bronchial carcinomas after implantation of an intrabronchial pellet in rats; further, calcium chromate induced injection-site sarcomas after intramuscular implantation in rats and mice and after intrapleural injection in rats. Bronchial carcinomas were produced in rats after intrabronchial implantation of strontium chromate and zinc chromate. Injection-site sarcomas were produced in rats and mice after intramuscular, intrapleural, and subcutaneous injections of chromite ore, strontium chromate, chromium trioxide, lead chromate, and zinc chromate, but few or no sarcomas were induced by barium chromate (CAS No. 10294-40-3), sodium chromate (CAS No. 7775-11-3), sodium dichromate (CAS No. 10588-01-9), or chromic acetate (CAS No. 1066-30-4) (IARC 1980, 1982, 1987).

PROPERTIES

Chromium is an odorless, steel to semi-gray, lustrous metal with oxidation states ranging from 2 to +6; however, the divalent (II), trivalent (III), and hexavalent (VI) forms are the most important. Elemental chromium (0) does not occur naturally. The divalent state (chromous) is readily oxidized to the more stable trivalent (chromic) state. The hexavalent (chromate) state is more stable than the divalent state, but is rarely found in nature. Hexavalent chromium compounds are strong oxidizers and are highly corrosive. They are generally reduced to the trivalent state in the environment. The solubility of hexavalent chromium compounds varies. Chromic acid, sodium chromate, and potassium chromate are soluble in water; calcium chromate and strontium chromate are slightly soluble; and zinc chromate and lead chromate are practically insoluble (ATSDR 2000).

Calcium chromate occurs in the form of yellow monoclinic prisms or a bright yellow powder. It is sparingly soluble in water, soluble in dilute acids, and reacts with acids and ethanol. Calcium chromate is probably nonflammable, but when heated to decomposition, it emits toxic fumes (HSDB 2001a, NTP 2001a). Chromium trioxide is a dark red or brown, deliquescent solid that occurs as prismatic crystals, flakes, or a granular powder. It is soluble in water, ethyl alcohol, ethyl ether, sulfuric acid, and nitric acid. Chromium trioxide is probably combustible and is a powerful oxidizer. Contact with organic chemicals may result in violent or explosive reactions (HSDB 2001b, NTP 2001b). Lead chromate occurs as yellow or orange monoclinic crystals. This compound is insoluble in water, acetic acid, and ammonia, but is soluble in dilute nitric acid and fixed alkali hydroxides. It is probably nonflammable, but reacts violently with ferric ferrocyanide (HSDB 2001c, NTP 2001c). Strontium chromate occurs as monoclinic yellow crystals. It is soluble in water, dilute hydrochloric acid, nitric acid, and acetic acid (HSDB 2001d). Zinc chromate occurs as lemon yellow prisms. It is insoluble in cold water and acetone, sparingly soluble in hot water, and soluble in acid and liquid ammonia (HSDB 2001e).

USE

The primary users of chromium include the metallurgical, refractory, and chemical industries. In 1976, the metallurgical industry accounted for approximately 59% of chromite ore use in the U.S., while the remainder was almost equally divided among the refractory and chemical industries. By 1987, the chemical and metallurgical industries accounted for approximately 91% of U.S. consumption, while use in the refractory industry declined to approximately 9% (IARC 1990). Chromium is used by the metallurgical industry to produce stainless steel, alloy cast steels, and nonferrous alloys. The refractory industry uses chromium to produce magnesite-chrome bricks and other materials used to line high temperature industrial furnaces. Hexavalent chromium compounds are widely used in the chemical industry in pigments, metal finishing, and wood preservatives. In 1996, approximately 52% of the chromium used in the chemical industry in the United States was used in wood preservatives (ATSDR 2000).

The steel industry is the major consumer of chromium. Chromium is used as an alloying and plating element on metal and plastic substrates for corrosion resistance in chromium containing and stainless steels and in protective coatings for automotive and equipment accessories. It is also used in nuclear and high-temperature research. The percentage of all U.S. chromium metal and metal alloys used to produce stainless steel increased from 70% in 1976 to 82% in 1987 (IARC 1990). In 1996, estimated consumption of chromium ferroalloys, metals, and other chromium-containing materials by end use was as follows: stainless and heat-resisting steel, 74%; full-alloy steel, 10%; superalloys, 3%; and other alloys, 13% (USGS 1997). Stainless steel and chromium alloys typically contain between 11.5% and 30% chromium (ATSDR 2000).

Hexavalent chromium compounds also are used in leather tanning, corrosion-resistance, textile dyeing, water treatment, inks, drilling muds, pyrotechnics, photography, process engraving, lithography, synthetic perfumes, and chemical synthesis. Calcium chromate is primarily used as a corrosion inhibitor and as a depolarizer in batteries. Chromium trioxide is used in chromium plating and other metal finishing operations, particularly in automobiles and military aircraft, as a wood preservative, as a corrosion inhibitor, as an oxidant in organic synthesis, and in catalyst manufacture. In 1978, 80% of the U.S. supply of chromium trioxide was used in metal treating and plating and only 10% was used in wood treatment. By 1988, 63% was used in wood treatment and 22% was used in metal finishing. Sodium chromate, and potassium chromate are used in the textile industry in various dyeing processes. Sodium

chromate is also used in inks, paints, leather tanning, wood preservation, corrosion inhibition, cuttings oils, and to produce other chromium compounds. Lead chromate was used in paints and printing inks and as a colorant in vinyls, rubber, and paper. In 1973, the U.S. EPA placed a ban on interstate shipments of paints for domestic use containing more than 0.06% lead. This ban reduced the demand for lead chromate pigments. Strontium chromate was initially used in artists' paints and for corrosion resistance on aluminum and magnesium alloys. It was also used in vinyl sheeting and chemical-resistant coatings. Similarly, zinc chromates are used as pigments in paints, varnishes, and oil colors; corrosion-resistant primer coatings; and as metal conditioners prior to priming (IARC 1973, 1990).

PRODUCTION

Chromite ore has not been mined in the United States since 1961. Domestic deposits are small or of low grade. Chromite ore, however, is imported in large quantities. Amounts ranging from approximately 273,000 to 476,000 metric tons per year (600 to 1,050 million lb) were imported between 1992 and 2000 (USGS 1997, 2001). The U.S. recycles scrap stainless steel as another source of chromium. Approximately 102,000 metric tons per year (224 million lb) were recovered, on average, between 1985 and 1999 (Kelly *et al.* 2001). Chromium metal, sodium chromate, and sodium dichromate are produced in the U.S. from imported chromite ore and most other chromium compounds are produced from sodium chromate and dichromate (ATSDR 2000).

The latest figures from the USITA show that approximately 632,500 lb of zinc and lead chromate were exported in 2000. The total export volumes for chromium trioxide; sodium dichromate; and other chromates, dichromates, and peroxchromates were approximately 25.6, 42.6, and 1.4 million lb, respectively. U.S. imports in 2000 for lead and zinc chromates, chromium trioxide, sodium dichromate, and other chromates, dichromates, and peroxchromates were 0.64, 17.7, 37.3, and 0.13 million lb, respectively (ITA 2001).

EXPOSURE

The primary routes of potential human exposure to chromium and certain chromium compounds are inhalation, ingestion, and dermal contact. Chromium (in the form of unidentified chromium compounds) is widely distributed in air, water, soil, and food. In trace amounts, the trivalent form is an essential ingredient in the diet. The entire population is possibly exposed to some of these compounds, but the levels of exposure vary. Hexavalent chromium compounds are of greater health concern than trivalent chromium compounds.

The National Occupational Hazard Survey, conducted by NIOSH from 1972 to 1974, estimated that 2.5 million workers were possibly exposed to chromium and its compounds in the workplace (NIOSH 1976). NIOSH estimated that 175,000 workers were potentially exposed to chromium (VI), which is produced principally from chromite ore (NIOSH 1979). The National Occupational Exposure Survey (NOES) (1981-1983) estimated that a total of 115,788 workers, including 3,101 women, were potentially exposed to chromium, and 6,339 total workers were potentially exposed to chromite ore (NIOSH 1984). The NOES also estimated that a total of 196,725 workers, including 31,444 women, were potentially exposed to hexavalent chromium (VI) compounds (barium chromate, calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate).

Chromium Hexavalent Compounds (Continued)

Occupational airborne chromium concentrations declined significantly during the past several decades because of improved emission controls. Occupational exposure, which can be two orders of magnitude greater than that to the general population, occurs primarily from stainless steel production and welding, chromate production, chrome plating, ferrochrome alloys, chrome pigment, and tanning industries. The typical concentration ranges of chromium (VI) in these industries are: stainless steel welding, 50 to 400 $\mu\text{g}/\text{m}^3$; chromate production, 100 to 500 $\mu\text{g}/\text{m}^3$; chrome plating, 5 to 25 $\mu\text{g}/\text{m}^3$; ferrochrome alloys, 10 to 140 $\mu\text{g}/\text{m}^3$; and chrome pigment, 60 to 600 $\mu\text{g}/\text{m}^3$ (ATSDR 2000). In a study assessing external and internal chromium exposure among stainless steel welders and mild steel welders, all chromium biological (blood, plasma, and urine) values were found to be higher among the former group, particularly those in the manual metal arc welding process. The higher levels are the result of very significant concentrations of total soluble chromium, mainly hexavalent chromium, in the fumes; the ratio of hexavalent soluble chromium to total water-soluble chromium was approximately 61% (Edm *et al.* 1997). In the tanning industry, exposure is almost exclusively to soluble chromium (III), typically in the range of 10 to 50 $\mu\text{g}/\text{m}^3$ (ATSDR 2000).

Between 1977 and 1984, typical total chromium concentrations in the ambient air in the U.S. was reported as $<0.01 \mu\text{g}/\text{m}^3$ in rural areas and 0.01 to 0.03 $\mu\text{g}/\text{m}^3$ in urban areas. Average atmospheric concentrations from more than 2,100 monitoring stations ranged from 0.005 to 0.525 $\mu\text{g}/\text{m}^3$. More recent studies from Hudson County, New Jersey reported an average background concentration of 0.0012 $\mu\text{g}/\text{m}^3$ for chromium (VI) in both indoor and outdoor air; however, concentrations were much more variable in indoor air (<0.001 to 3 $\mu\text{g}/\text{m}^3$) compared to outdoor air (<0.001 to 0.0038 $\mu\text{g}/\text{m}^3$). A survey of more than 3,800 tap water samples in 1974 and 1975 found chromium concentrations ranging from 0.4 to 8.0 $\mu\text{g}/\text{L}$ with a mean value of 1.8 $\mu\text{g}/\text{L}$. Surveys of U.S. surface waters indicate that chromium concentrations in rivers range from <1 to 30 $\mu\text{g}/\text{L}$, while concentrations in lakes are typically $<5 \mu\text{g}/\text{L}$. Typical chromium levels in most fresh foods are low. Chromium has been detected in vegetables, fruits, grains, cereals, eggs, meat, and fish at concentrations between 20 and 520 $\mu\text{g}/\text{kg}$ (ATSDR 2000).

The general population can be exposed to chromium through the air, water, soils and food. The mean daily dietary intake of chromium from air, water, and food is approximately <0.2 to 0.6, <4 , and 60 μg , respectively. Dermal exposure may occur through contact with wood treated with chromated copper arsenate or other consumer products that contain chromium. People who live near waste sites or industrial facilities that release chromium to the environment would have a higher probability of chromium exposure (ATSDR 2000).

EPA's Toxic Chemical Release Inventory (TRI) listed 2,022 and 1,774 industrial facilities that produced, processed, or otherwise used chromium or chromium compounds, respectively, in 1999. The facilities reported releases of chromium and chromium compounds to the environment which were estimated to total approximately 29 and 174 million lb, respectively. Approximately 90% of the total releases were reported by the top 100 facilities. Environmental releases of chromium and chromium compounds did not show any consistent trends between 1988 and 1999 (TRI99 2001).

REGULATIONS

In 1982, the U.S. Consumer Product Safety Commission (CPSC) investigated the potential hazard to consumers from chromium-containing inks, printed products, and nonprinted consumer products. Although chromium was present in some inks used in printed products, the levels found in the final products did not warrant further investigation.

Chromium Hexavalent Compounds (Continued)

EPA regulates chromium hexavalent compounds under the Clean Water Act (CWA), Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Resource Conservation and Recovery Act (RCRA), Superfund Amendments and Reauthorization Act (SARA), and Toxic Substances Control Act (TSCA). The CERCLA reportable quantities (RQs) for chromium and some chromium compounds are 1 lb (0.454 kg), while the RQs for calcium chromate and strontium chromate are 10 lb (4.54 kg). EPA, under RCRA, SARA, and CERCLA, subjects chromium and its compounds to reporting and record-keeping requirements. Particles of chromium greater than 100 micrometers (0.004 inches) are exempt from reporting under CERCLA. EPA's Carcinogen Assessment Group includes 10 chromium compounds on its list of potential carcinogens.

FDA regulates the use of chromium as indirect food and color additives, in beverages, and in dental devices, and chromic oxide in drugs and cosmetics.

NIOSH recommends an exposure limit of 0.001 mg/m³ as a 10-hour time weighted average for chromium and hexavalent chromium (VI) and recommends an exposure limit of 500 µg/m³ as a 10-hr time-weighted average (TWA) for chromium (II and III) compounds and chromium metal. OSHA has set an 8-hr TWA permissible exposure limit (PEL) of 0.5 mg/m³ for chromium(II) and chromium(III) compounds and 1 mg/m³ for chromium metal; for chromic acid and chromate, the PEL varies with the compound. A ceiling of 0.1 ppm, however, is given. OSHA also regulates chromium hexavalent compounds under the Hazard Communication Standard and as chemical hazards in laboratories. Regulations are summarized in Volume II, Table 45.

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